COATINGS. ENAMELS

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PARTICULARS OF THE BEHAVIOR OF GAS INCLUSIONS IN BASE AND COVERING ENAMELS DURING FIRING

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A qualitative analysis of the motion of an individual gas bubble through the transition layer between base and covering enamels under a surface tension gradient is performed. The velocity of gas inclusions moving by a thermodynamic mechanism and by a flow mechanism is evaluated.

Key words: gas bubble, base enamel, covering enamel, firing, macrostructure, film liquid, Marangoni effect, surface tension, iron oxide, capillary motion, surface tension gradient.

During relatively rapid firing of enamel a nonuniform oxide glassy film forms on a metallic surface with a corresponding macrostructure. An ordinary enamel coating consists of two or more layers with different composition and functional characteristics. In addition, the interaction of the base enamel with the metal changes the contact concentrations of the components of the enamels because of exchange reactions in which binding oxides participate. For this reason, the surface tension σ of gas inclusions present (bubbles) in an enamel layer is different on different sections of the melt – gas interface.

A surface tension difference causes a liquid film on a surface to flow provided that it can move (Marangoni effect). The shear stress in the boundary film (grad σ) is similar to a hydrostatic pressure difference in a simple liquid. Just as a bulk liquid flows under the action of the pressure difference in the direction of lower pressure, when a gradient of the surface tension σ arises a film liquid flows in the direction of higher surface tension (Fig. 1). The spontaneous flow of film liquid lowers the Gibbs energy of the system, increasing the surface area with lower surface tension.

Therefore, the mechanism of the motion of gas inclusions in enamels under a gradient of an interface tension reduces to flow of a free boundary film together with a layer of the adjoining liquid from any part into the back part and to a corresponding movement of a gas inclusion itself in the opposite direction. The moving outer liquid transfers a suspended bubble to a new position corresponding to a lower energy of the system (Fig. 2).

When the base enamel is fired the composition of the contact layer of oxide melt changes [1]; the iron oxide (Fe_2O_3) content changes from the initial value to 10%[3] or more. The experimental dependence of the surface tension on the iron oxide content is presented in Fig. 3.

According to this dependence, as the Fe_2O_3 content increases to 9% the surface tension decreases. This behavior of the curve $\sigma = \sigma(Fe_2O_3)$ corresponds to a change of the surface tension over the cross section of the base enamel

[3] Here and below — content by weight.

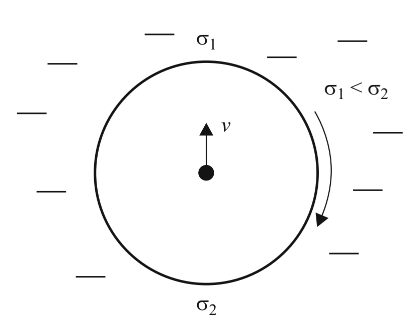

Fig. 1. Mechanism of the motion of gas inclusions (Marangoni effect): σ) surface tension of the liquid; v) velocity of the bubble.

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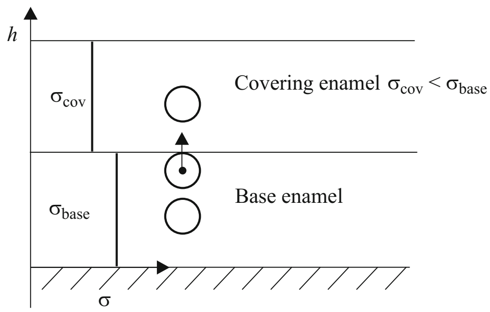

Fig. 2. Ratio of the surface tension σ_{base} of the base enamel and that σ_{cov} of the covering enamel when they are both deposited at the start of firing ($\tau = 0$).

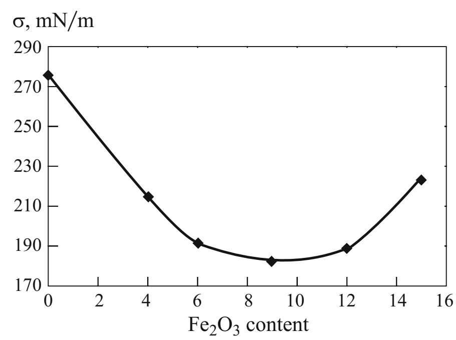

Fig. 3. Surface tension of a base layer of enamel versus the iron oxide (Fe_2O_3) content.

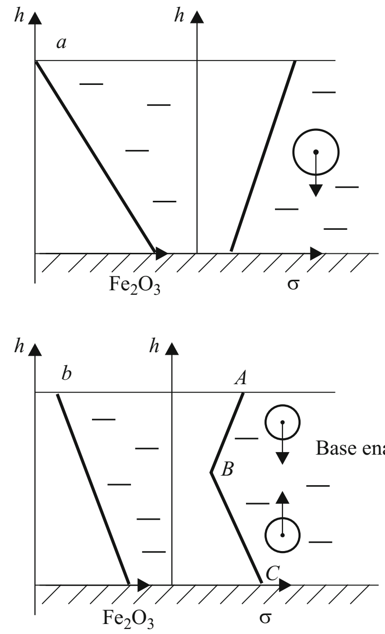

Fig. 4. Change of Fe_2O_3 content and surface tension over the section h of the base enamel layer: a, b) start and completion of firing, respectively.

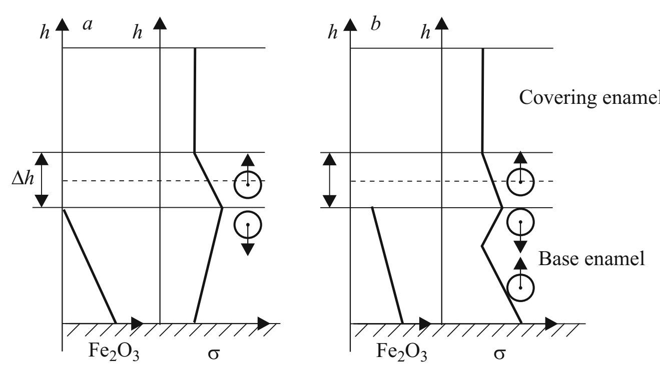

Fig. 5. Change of Fe_2O_3 content and of the surface tension over the section h of the enamel layer with combined deposition of the base and covering enamels: a, b) start and completion of firing, respectively; Δh) thickness of the transitional layer.

(Fig. 4*a* and in Fig. 4*b*, segment *AB*). Therefore, bubbles move toward the surface of the metal when the content of iron oxide is low. When the Fe_2O_3 iron content increases to above 9% the surface tension increases (see Fig. 4*b*, segment *BC*). As a result, at elevated Fe_2O_3 content the bubble detaches from the surface of the metal and its capillary motion is upwards.

In the combined method of depositing base and covering layers of enamel (technology 2S/1B), after a definite period of time a transitional (intermediate) layer of enamel with thickness *l* forms at the interface of the layers (Fig. 5). This layer becomes thicker with time. Simultaneously with this process, the gradient of the surface tension in the base enamel changes as a result of an increase in the Fe_2O_3 content. In this case, at the start of firing the surface tension assumes the form of the curve shown in Fig. 5*a* and at the completion of firing it assumes the form shown in Fig. 5*b*. A bubble strives to occupy an energetically favorable position with a lower surface tension and passes through the intermediate layer into the covering enamel.

The qualitative analysis pertains to the simple case of the motion of an individual gas bubble. In a real situation many gas bubbles move parallel to one another with different velocities. Since such motion is a result of the flow of a film of liquid, the iron oxide content in neighboring bubbles is always changing. In some cases this effect can accelerate the motion and in other cases it can retard the motion or even change the direction of motion. For this reason, the particulars noted above must be taken into account in the case of an ensemble of gas inclusions.

To calculate the velocity of a bubble through the transitional layer the thickness Δh of the film was taken to be 0.05, 01.0, and 0.15 mm, and the bubble radius r was taken to be 0.02, 0.04, 0.06, and 0.08 mm.

The velocity of gas bubbles as a result of a surface tension gradient by a thermodynamic mechanism and by the film-flow mechanism was evaluated [1]. The dependences obtained are presented in Fig. 6.

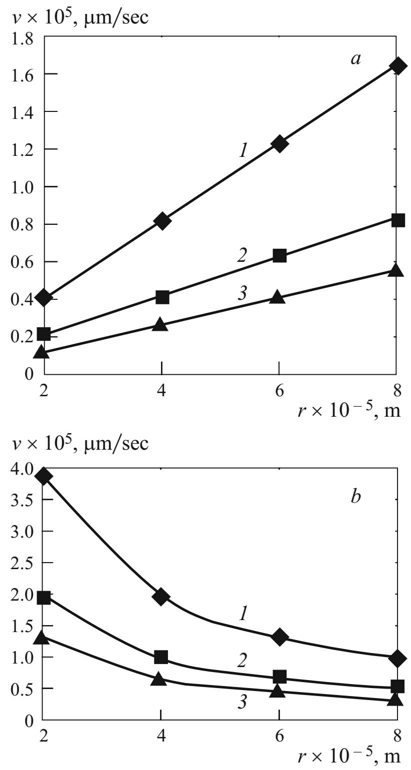

Fig. 6. Velocity of gas inclusions versus their size, calculated using the thermodynamic mechanism (*a*) and the film-flow mechanism (*b*) with $\Delta h = 5 \times 10^{-5}$, 10×10^{-5}, and 15×10^{-5} m (*1*, *2*, and *3*, respectively).

Firing gives rise to many dynamic physical – chemical processes in the complex composite system enamel – metal, but these processes never reach thermodynamic equilibrium. So, the content of iron oxides should not exceed a critical value at which crystallization processes start. Not only chemical interactions but also possible viscous flows of enamel melt participate.

Film flow is found to be most effective for small gas bubbles. Here, the inverse dependence on the size of inclusions is observed.

To prevent denuding of the base enamel layer as a result of the Marangoni effect, the surface tension of this layer must be higher than that of the covering melt. Outflow of the lower layer of enamel is prevented in a similar manner. The capillary flow of an enamel film on the surface of a gas bubble because of a gradient of the surface tension gives rise to film flow. The motion of gas inclusion which was examined above is a manifestation of the Marangoni effect.

REFERENCES

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